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THE SYNTHESIS OF UNSATURATED FLUOROCARBONS

**Supported in part by Wright Air Development Division
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Between

The Office of the Quartermaster General

and

The University of Florida

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John Savory**

I. INTRODUCTION

The purpose of this project is to conduct the necessary research for the preparation of unsaturated organic compounds containing fluorine and, when synthetic methods have been developed, to prepare various fluoro-olefins which may give elastomers which are oil and fuel resistant and which retain their elasticity at low temperatures.

It is estimated that 93% of the work has been completed to date and that 92% of the estimated costs have been incurred to date.

This research is authorized under Contract Number DA-19-129-QM-500 and is a further continuation of the work initiated under DA-44-109-QM-522 and continued under DA-44-109-QM-1469. The Wright Air Development Center has contributed funds for the operation of the project in part since September 13, 1956, under MIPR 33(616)-5701.

This is the 27th quarterly report under the contract but the 44th since the project was initiated in 1951. The period covered is from March 13, 1962, through June 13, 1962.

II. SUMMARY OF CURRENT PROGRESS

$\text{CF}_2=\text{CH}-\text{CF}_2\text{NO}$ and $\text{CF}_2=\text{CF}-\text{CF}_2\text{NO}$ have been prepared in 24.5% and 34% yield respectively by reacting the corresponding polyfluoroallyl iodide with nitric oxide in the presence of mercury.

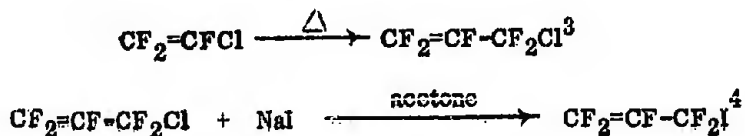
Polyfluoroallyl chlorides and iodides react with nitrogen dioxide in the presence of mercury to give high yields of the corresponding polyfluoroacrylic acid fluorides.

III. DISCUSSION

The previous report from this laboratory¹ has described the reaction carried out in a 1 liter Vycor Flask when $\text{CF}_2=\text{CH}-\text{CF}_2\text{I}$, nitric oxide, and mercury were subjected to ultraviolet irradiation for 4 hours.

A low yield of $\text{CF}_2=\text{CH}-\text{CF}_2\text{NO}$ was obtained and it was noted that this was probably due to over-irradiation. A similar reaction was therefore carried out over a 25 minute period using ultraviolet irradiation from a Hannoveria SH burner. The main products were $\text{CF}_2=\text{CH}-\text{CF}_3$ and $\text{CF}_2=\text{CH}-\text{COF}$ with only a trace of $\text{CF}_2\text{CH}-\text{CF}_2\text{NO}$. Unreacted nitric oxide was removed in this case and in all subsequent reactions by introduction of oxygen with which it forms nitrogen dioxide; mercury then reacts with the latter to give mercuric nitrate and nitric oxide.² It appeared that again the reaction was over-irradiated; therefore, all subsequent reactions were carried out in a 2 liter pyrex flask using sunlight as a source of ultraviolet irradiation. $\text{CF}_2=\text{CH}-\text{CF}_2\text{I}$ was reacted under these conditions for periods of irradiation ranging from 2 minutes to 105 minutes. The maximum yield of $\text{CF}_2=\text{CH}-\text{CF}_2\text{NO}$, 24.5%, was obtained after the longest period of irradiation.

$\text{CF}_2=\text{CH}-\text{CF}_2\text{I}$ was prepared by the following known reaction scheme:



This allyl iodide was subjected to the same reaction conditions as the $\text{CF}_2=\text{CH}-\text{CF}_2\text{I}$ for periods of irradiation up to 6 hours. A maximum yield of 34% of $\text{CF}_2=\text{CF}-\text{CF}_2\text{NO}$ was obtained. This latter compound was stable for several weeks at -78°C ., but at room temperature it decomposed completely after 3 days to give a brown oil and some relatively volatile colorless liquid. $\text{CF}_2=\text{CH}-\text{CF}_2\text{NO}$ slowly decomposed at -78°C and at room temperature was only stable for a few hours.

The other main products from the reactions of $\text{CF}_2=\text{CH}-\text{CF}_2\text{I}$ and $\text{CF}_2=\text{CF}-\text{CF}_2\text{I}$ with nitric oxide and mercury were the corresponding fluoro-olefins and acrylic acid fluorides $\text{CF}_2=\text{CX}-\text{CF}_3$ and $\text{CF}_2=\text{CX}-\text{COF}$ ($\text{X}=\text{H}, \text{F}$).

The yield of acrylic acid fluoride increased with decreasing length of irradiation. This meant that some reaction other than fluoroallyliodide with nitric oxide was occurring. The introduction of oxygen in the later stages of reaction converted nitric oxide into nitrogen dioxide and it was after this point that the acrylic acid fluoride was formed. Reaction between $\text{CF}_2=\text{CF}-\text{CF}_2\text{I}$ and oxygen resulted in a violent explosion; substitution of air for oxygen gave no reaction. $\text{CF}_2=\text{CF}-\text{CF}_2\text{I}$ and nitrogen dioxide, however, gave $\text{CF}_2=\text{CF}-\text{COF}$ in 81% yield. It was found necessary, in this reaction, to have an agitated pool of mercury in the flask, otherwise; only a negligible amount of acid fluoride was obtained. Thus an explanation was obtained for the formation of acrylic acid fluorides in all reactions carried out between either $\text{CF}_2=\text{CH}-\text{CF}_2\text{I}$ or $\text{CF}_2=\text{CF}-\text{CF}_2\text{I}$, and nitric oxide; in all cases nitrogen dioxide had been present in the working up procedure. As an extension to this reaction $\text{CF}_2=\text{CH}-\text{CF}_2\text{Cl}$ was reacted with nitrogen dioxide giving $\text{CF}_2=\text{CH}-\text{COF}$ in a 93% yield. This reaction was carried out in the presence of oxygen, which converts any NO

formed, by the reaction of mercury with NO_2 , back into NO_2 . $\text{CF}_3\text{CF}_2\text{CF}_2\text{I}$ did not react at all under these conditions.

A series of continuous flow reactions between $\text{CF}_2=\text{CF}-\text{CF}_2\text{I}$ and NO were carried out. Passage through a long Vycor tube under ultraviolet irradiation, bubbling through mercury also under ultraviolet irradiation, and bubbling through mercury at 100° all gave chiefly unreacted $\text{CF}_2=\text{CF}-\text{CF}_2\text{I}$. A trace of $\text{CF}_2=\text{CF}-\text{CF}_2\text{NO}$ was indicated by analytical V. P. C. in the product from the second continuous flow reaction.

IV. EXPERIMENTAL

Reactions between Polyfluoroallyliodides and Nitric Oxide

3-Iodo-1,1,3,3-Tetrafluoropropene

A 2 liter pyrex flask containing mercury (70 mls.) was evacuated and charged with 3-iodo-1,1,3,3-tetrafluoropropene (4.8 g., 0.02 mole), nitric oxide (1.2 g., 0.04 mole) and mechanically shaken in bright sunshine for 105 minutes. The flask was cooled in ice water, oxygen (1.28 g., 0.04 mole) was introduced, and the flask shaken for an additional 30 minutes. Volatile material was isolated by slowly pumping through two traps cooled in liquid nitrogen. This mixture was separated by large scale V. P. C. using dinonylphthalate as the stationary phase at room temperature, nitrogen flowrate 200 mls./min. into: 2H-pentafluoropropene (1.0 g., 38% yield), an infrared spectrum was identical with that of an authentic sample; 3-nitroso-1,1,3,3-tetrafluoropropene (0.7 g., 24.5% yield. Found: M. 142 $\text{C}_3\text{HF}_4\text{NO}$ requires M. 143) an infrared spectrum showed $\text{C}=\text{C}$ and NO stretching absorptions at 5.71 (vs) and 6.29 (m), and bands at 7.30 (s), 7.9 (m)

and 8.1 (m), 8.9 (ms), 9.7 (w), and 10.5 (m) μ ; nuclear magnetic resonance data was in concord with the formulation $\text{CF}_2=\text{CF}-\text{CF}_2\text{NO}$; and β,β -difluoroacryloylfluoride (0.7 g., 32% yield), b.p. 45.0°C . (Found: C, 32.55; F, 51.60; H, 0.81%. $\text{C}_3\text{HF}_3\text{O}$ requires C, 32.73; F, 51.82; H, 0.91%.) Molecular weight, infrared and N. M. R. data on this compound were reported in the previous report.¹

Perfluoroallyliodide

Perfluoroallyliodide was prepared from perfluoroallyl chloride as described by Miller and Fainberg.⁴ Perfluoroallylchloride was prepared by the pyrolysis of chlorotrifluoroethylene as described by Miller.³

Perfluoroallyliodide (5.16 g., 0.02 mole) was reacted similarly in bright sunshine for 6 hours. Separation of the products gave: Perfluoropropene (0.6 g., 20% yield), identified by its infrared spectrum; 3-nitrosoperfluoropropene (1.1 g., 34% yield; Found: M. 161; C, 22.66; N, 8.60; F, 58.68; $\text{C}_3\text{F}_5\text{NO}$ requires M. 161; C, 22.39; N, 8.70; F. 59.00%) an infrared spectrum showed C=C and NO stretching absorptions at 5.61 (vs) and 6.29 (s) μ , and bands at 7.30 (vs), 7.58 (vs), 8.40 (vs), 9.18 (vs), 10.5 (w), 11.1 (w), and 13.9 (w); and perfluoroacryloyl-fluoride (0.7 g., 27.5 % yield Found: M, 128; C, 28.35; F, 59.12. $\text{C}_3\text{F}_4\text{O}$ requires M. 128; C, 28.13; F, 59.37%) an infrared spectrum showed C=C and C=O stretching absorptions at 5.40 (vs) and 5.72 (vs) and bands at 7.3 (s), 7.55 (s), 8.41 (s), (9.50 (ms), 9.75 (s) and 9.80 (s) μ (doublet); nuclear magnetic resonance data confirmed the formulation $\text{CF}_2=\text{CF}-\text{COF}$ for this compound.

Varying conditions for these reactions are summarized in Table I.

Continuous Flow Reactions between Perfluoroallyliodide and Nitric Oxide

Oxygen free nitrogen was obtained by passing cylinder nitrogen over hot copper wire. Nitric oxide was partially purified by bubbling through mercury. The perfluoroallyl iodide (5.16 g., 0.02 mole) was passed through the reaction zone by being entrained in a stream of nitrogen (flowrate 30 mls./minute). This stream of nitrogen plus perfluoroallyl iodide and the stream of nitric oxide (flowrate 15 mls./minute) were mixed before passing through the reaction zone.

Reaction 1

The reactants were passed through a Vycor tube (92 cms. long, 7 mm. diameter) which was under ultraviolet irradiation from 3 Hannovia SH burners. Volatile material other than nitric oxide was collected in 2 cold traps (-78°) and was shown by analytical V. P. C. to contain only unreacted perfluoroallyl iodide; an infrared spectrum confirmed this.

Reaction 2

The reactants were bubbled through mercury (30 mls.) contained in a pyrex trap which was irradiated with two ultraviolet lamps. The material collected in the two cold traps was introduced onto a large scale V. P. C. column (D. N. P. 25°) and shown to contain traces of hexafluoropropene, 3-nitrosoperfluoro-propene, perfluoroacryloyl fluoride all of which were identified by retention times. Unreacted perfluoroallyl iodide (4.9 g.) was recovered.

Reaction 3

Reaction 2 was repeated except that the mercury instead of being irradiated was heated to 100° . Analytical V. P. C. and infrared analysis showed that no reaction had occurred.

Reaction 4

The Vycor tube used in reaction 1 was bent into a triple - u shape with about 2 mls. of mercury at the bottom of each "u".

The reaction mixture was passed through this tube which was irradiated by three ultraviolet lamps. Mercury iodide and oxide quickly coated the surface of the tube thus stopping ultraviolet transmission and therefore reaction. An analytical V. P. C. (dibutyl sebacate 25° and 60°) investigation on the product indicated that it consisted of almost completely unreacted perfluoroallyl iodide together with a trace of 3-nitrosoperfluoropropene.

Reaction between Perfluoroallyliodide and Oxygen

Perfluoroallyliodide (5.1 g., 0.02 mole), oxygen (1.89 g., 0.059 mole) and mercury (70 mls.) were introduced into a 2 liter pyrex flask and shaken in the dark. A violent explosion occurred after 15 minutes.

The same result was observed in a similar reaction when aliquots (50 mm.) of oxygen were introduced at 5 minute intervals. The explosion occurred after 12 minutes.

In a final reaction aliquots (100 mm.) of dry air were introduced into the flask, one initially and one after 10 minutes shaking. Shaking was continued for 90 minutes when volatile material (4.7 g.) was removed under vacuum and identified, by its infrared spectrum, as recovered perfluoroallyliodide.

Reaction between Organic Fluorohalides and Nitrogen Dioxide

Perfluoroallyliodide

A 2 liter pyrex flask containing mercury (70 mls.) was charged under vacuum with perfluoroallyliodide (5.16 g., 0.02 mole) nitrogen dioxide (1.39 g.,

0.03 mole), and shaken in the dark for 1 hour when all brown vapor had disappeared. Volatile material was removed under vacuum and was observed to contain some nitric oxide which boiled away when the product mixture was warmed to -78°C . Large scale V. P. C. separation (dinonylphthalate, 23°C .) gave perfluoropropene (0.25 g., 11% yield), 3-nitrosoperfluoropropene (0.15 g., 6% yield), perfluoroacryloyl fluoride (1.55 g., 81% yield) and recovered perfluoroallyliodide (1.0 g., 75% conversion). All compounds were identified by identical infrared spectra with those of authentic samples.

A similar reaction was carried out without shaking the flask. Only unreacted perfluoroallyliodide (4.8 g.) was recovered.

3-Chloro-1,1,3,3-tetrafluoropropene

3-Chloro-1,1,3,3-tetrafluoropropene (2.98 g., 0.02 mole), nitrogen dioxide (1.38 g., 0.03 mole) and oxygen (0.96 g., 0.03 mole) were reacted similarly with mercury (70 mls.). Recovered 3-chloro-1,1,3,3-tetrafluoropropene (0.3 g., 90% conversion) and β,β -difluoroacryloyl fluoride (1.85 g., 93% yield) were obtained together with traces of 2H-pentafluoropropene and 3-nitroso-1,1,3,3-tetrafluoropropene. The two main products were identified by their infrared spectra and the last two by their retention times on analytical V. P. C.

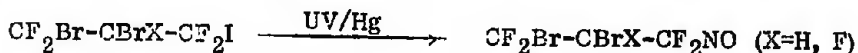
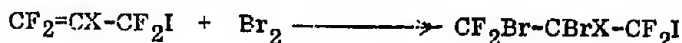
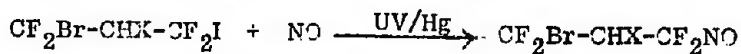
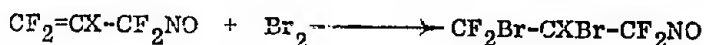
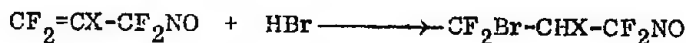
Heptafluoro-1-iodopropane

Heptafluoro-1-iodopropane (5.9 g., 0.02 mole), nitrogen dioxide (1.38 g., 0.03 mole) oxygen (0.96 g., 0.03 mole) and mercury (55 mls.) were shaken for 1 hour in a 2 liter flask. Recovered heptafluoro-1-iodopropane (5.5 g.), identified by its infrared spectrum, was the only volatile material obtained.

V. FUTURE WORK

A determination of the half-lives at room temperature of $\text{CF}_2=\text{CHCF}_2\text{NO}$ and $\text{CF}_2=\text{CF}-\text{CF}_2\text{NO}$ will be carried out, and the identity of some of the decomposition products established.

The synthesis of other fluorine-containing nitroso compounds by the following methods will be attempted:



The addition of nitrosyl chloride to a variety of fluoro-olefins will also be carried out.

VI. FUTURE WORK

1. Paul Tarrant and John Savory, Quarterly Report 43.
2. E. Divers and T. Shimidzu, J. C. S., 47, 630, (1885).
3. W. T. Miller, U. S. P. 2733277 (1956).
4. W. T. Miller and A. H. Fainberg, J. A. C. S., 79, 4164 (1957).

<p>AD _____ Accession No. _____</p> <p>Department of Chemistry, University of Florida, Gainesville, Florida</p> <p>SYNTHESIS OF CERTAIN TYPES OF UNSATURATED FLUOROCARBONS - Paul Tarrant, John Savory July, 1962, 10 pp. (Quarterly report 44)</p> <p>Unclassified report</p> <p>$CF_2=CH-CF_2NO$ and $CF_2=CF-CF_2NO$ have been prepared in 24.5% and 34% yield respectively by reacting the corresponding polyfluoroallyl iodide with nitric oxide in the presence of mercury.</p> <p>Polyfluoroallyl chlorides and iodides react with nitrogen dioxide in the presence of mercury to give high yields of the corresponding polyfluoroacrylic acid fluorides.</p>	<p>AD _____ Accession No. _____</p> <p>Department of Chemistry, University of Florida, Gainesville, Florida</p> <p>SYNTHESIS OF CERTAIN TYPES OF UNSATURATED FLUOROCARBONS - Paul Tarrant, John Savory July, 1962, 10 pp. (Quarterly report 44)</p> <p>Unclassified report</p> <p>$CF_2=CH-CF_2NO$ and $CF_2=CF-CF_2NO$ have been prepared in 24.5% and 34% yield respectively by reacting the corresponding polyfluoroallyl iodide with nitric oxide in the presence of mercury.</p> <p>Polyfluoroallyl chlorides and iodides react with nitrogen dioxide in the presence of mercury to give high yields of the corresponding polyfluoroacrylic acid fluorides.</p>
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